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AMINO ACID RACEMISATION DATING OF A RAISED GRAVEL BEACH DEPOSIT, SELLICKS BEACH, SOUTH AUSTRALIA

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Summary

Murray-Wallace, C.V. & Bourman, R.P. (2002). Amino acid racemisation dating of a raised gravel beach deposit, Sellicks Beach, South Australia. *Trans. R. Soc. S. Aust.* **126** (1), 21-28, 31 May, 2002.

The extent of racemisation (total acid hydrolysate) of the amino acids aspartic acid, glutamic acid, leucine, phenylalanine and valine indicates a minimum age of last interglacial for fossil molluscs occurring within a raised gravel beach deposit at Sellicks Beach, South Australia. The base of the raised gravel beach occurs up to 5.5 m above Australian Height Datum (AHD) and possibly indicates 3 m of local uplift since the last interglacial maximum (c. 125 ka; Oxygen Isotope Substage 5e). Emergence of the gravel beach is attributed to ongoing neotectonic uplift of Fleurieu Peninsula.

Key Words: amino acid racemisation, last interglacial, neotectonics, sea-levels, South Australia.

Introduction

A resurgence of interest in recent years in Quaternary emergent shoreline successions has arisen from the increasing ability to determine the age of these features due to technological advances in geochronology (Rutter & Catto 1995; Noller *et al.* 2000). Similarly, an increasing awareness that coastal successions, particularly those deposited during the last interglaciation (c.125 ka), are sufficiently old to quantify even modest rates of neotectonism, has bolstered this research endeavour. Accordingly, the elevation of last interglacial coastal deposits has been widely used as a benchmark to delineate recent teetonic behaviour at continental scales (Murray-Wallace & Belperio 1991; Ota 1994; Bourman *et al.* 1999; Zazo *et al.* 1999). In this work, the age of a raised beach deposit at southern Sellicks Beach, South Australia, is determined based on the extent of racemisation of several amino acids within molluscs from the fossil assemblage. In addition, the neotectonic significance of this deposit and its relation to other emergent shoreline deposits on Fleurieu Peninsula is examined.

Materials and Methods

Field investigations

The elevation and lateral extent of the gravel beach deposit was surveyed to Australian Height Datum (AHD) using an automatic level. In addition to a general field description of the deposit, shell samples were collected for amino acid racemisation dating and to document the fossil mollusc assemblage. Species identification followed that set out in Ludbrook (1984).

Amino acid racemisation analyses

Samples of fossil molluscs for amino acid racemisation analyses (total acid hydrolysate) were collected from the gravel beach deposit. Shells were removed from the matrix of the deposit and their depth of burial recorded. Analyses were undertaken on specimens of *Patella (Scutellastra) laticostata* Blainville, *Thais orbita* (Gmelin), *Sydaphera undulata* (Sowerby), *Nerita (Melanerita) atramentosa* Reeve and *Ostrea* sp. Linnaeus.

Sediment adhering to the surfaces of shell samples and diagenetically modified aragonite, particularly chalky surfaces, were removed with a dental drill, followed by successive washes in distilled water using an ultrasonic bath. A dilute acid etch (2 mol HCl) was subsequently undertaken to remove the outer surfaces (c. 10-15% by mass) of the shells that had been in contact with the host sediment. Samples were subsequently hydrolysed for 22 hours at 110° C in 8 mol HCl. Following cation exchange isolation of the amino acid residues, samples were freeze dried and derivatized. Chromatography of the N-penta-fluoropropionyl D, L-amino acid 2-propyl esters was performed using a Hewlett-Packard 5890A Series II gas chromatograph with a flame ionisation detector and a 25 m coiled, fused silica capillary column coated with the stationary phase Chirasil-L-Val. Full details of the analytical techniques followed in this work are reported elsewhere (Murray-Wallace 1993). Enantiomeric ratios were determined for the amino acids aspartic acid (ASP), glutamic acid (GLU), leucine (LEU), phenylalanine (PHE) and valine (VAL).

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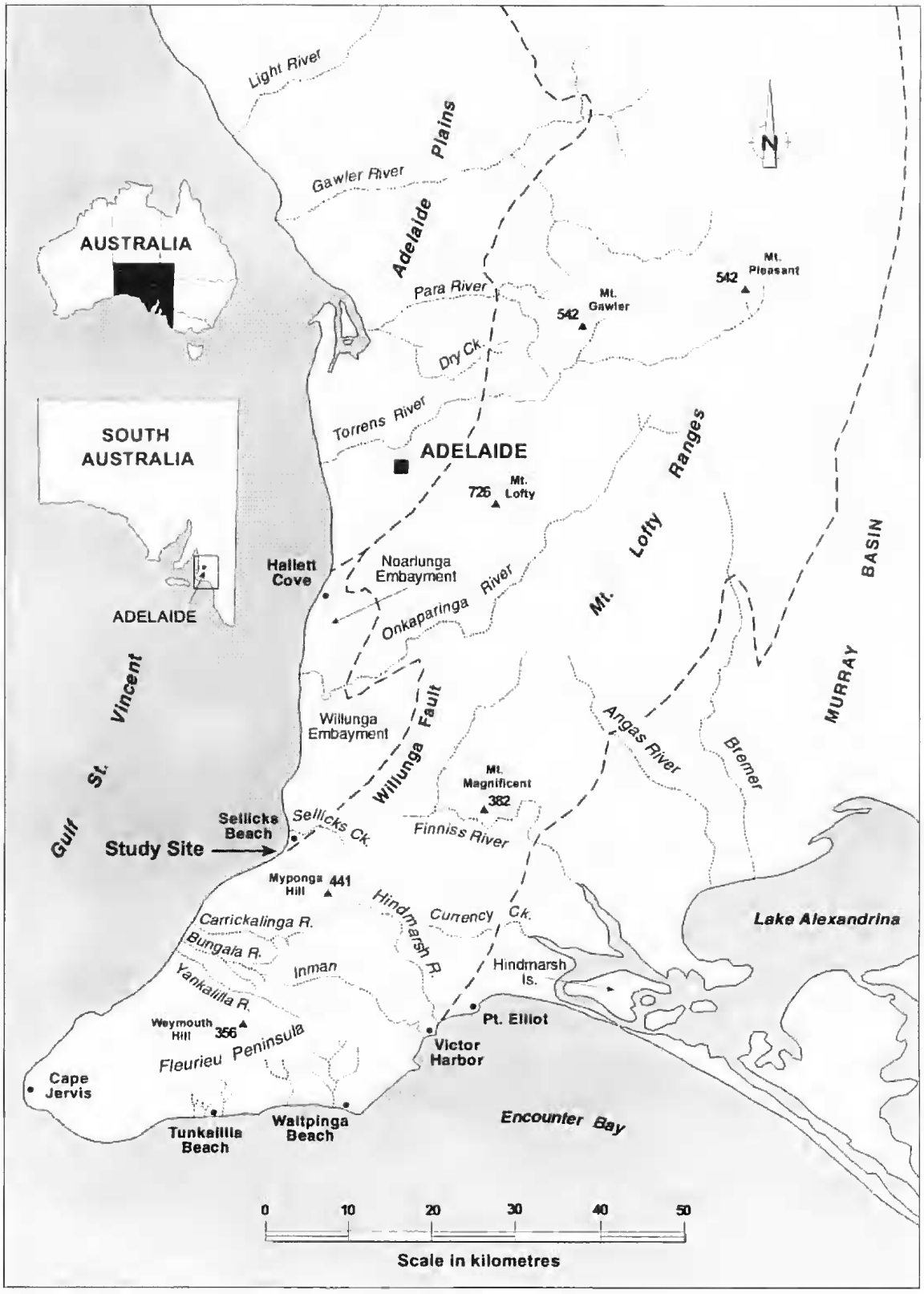

Fig. 1 Location of the raised gravel beach deposit, Sellicks Beach, South Australia.

Fig 2. View looking south along southern Sellicks Beach towards the southern Adelaide Hills and coastal cliffs developed on Pleistocene alluvial fan successions. The location of the raised beach deposit, which occurs in the scarp foot zone is indicated by an arrow.

Fig. 4. A shore-normal view of the raised gravel beach deposit at Sellicks Beach. The steeply dipping Ochre Cove Formation is visible near the survey staff. The staff, which is fully extended, is 5 m long.

Geomorphological Setting And Site Description

The raised gravel beach deposit is situated near the Willunga Fault at the southern-most part of Sellicks Beach (35° 21' 09.8" S; 138° 26' 07.5" E), landward of a modern, gently seaward sloping intertidal shore platform (Figs 1, 2). The modern intertidal platform is approximately 20 m wide in a shore-normal transect, is partially covered with boulders and cobbles and represents a modern analogue for the relict platform (Fig. 3). An accumulation of boulders and cobbles occurs at the foot of the modern cliff and represents a further modern analogue of the raised beach deposit. The emergent gravel beach facies rests on a strongly eroded remnant of a shore platform that is developed on the steeply dipping Oligo-Miocene Port Willunga Beds (Daily *et al.*

Fig. 3. View looking southwest towards the raised gravel beach deposit at Sellicks Beach. The gravels rest unconformably on the Oligo-Miocene Port Willunga Beds and the Middle Pleistocene Ochre Cove Formation. The gravel deposit dips gently seawards. The unconformity surface represents a relict intertidal shore platform. The modern intertidal platform occurs in the foreground, dips gently seaward and is partially covered by boulders and cobbles. The maximum difference in elevation between the two platforms is 5 m as determined in the most landward exposure, not visible in this photograph. Small, isolated, sea stacks representing erosional remnants of the formerly more extensive Pleistocene shore platform occur within this area (e.g. "a" in the middle distance).

1976), and in part, a steeply dipping portion of the Middle Pleistocene Ochre Cove Formation (Ward 1966; Pillans & Bourman 1996; Figs 3, 4, 5). The gravel deposit occurs within a former scarp foot zone excavated at a time of higher sea level, and abuts fanglomerates of the Ochre Cove Formation (May & Bourman 1984).

The bedrock surface on which the gravel beach facies rests, grades in a seaward direction from 5.55 m to 4.95 m above Australian Height Datum (AHD). The platform extends out seaward from the deposit some 1-1.5 m forming a well-defined bench (Fig. 6). The gravel beach facies crops out over a shore-parallel distance of approximately 50 m, and ranges in thickness between 1 and 1.5 m (Fig. 6).

The gravel deposit is poorly sorted and comprises sub-rounded to subangular clasts of siltstone, quartzite and bryozoal limestone that range from boulder to pebble size, although the modal clast size is boulder-cobble (700-70 mm). The lithoclasts are tightly packed. Numerous entire and fragmental fossil molluscs occur within the granular matrix of the gravel deposit.

A pale grey, clean, free-flowing sand is thinly draped over the gravel deposit and the underlying fanglomerates and extends up to 2.5 m above the upper bounding surface of the deposit. The sand also

Fig. 5. Detail from figure 4 showing the tightly packed arrangement of lithoclasts.

Fig. 6. View looking eastnortheast showing part of the shore-parallel lateral extent of the raised beach deposit. The letter "a" denotes the general level of the gravel deposit which is approximately 4 m above the gravel covered footslope of the small cliff in the foreground. A planated surface representing remnants of an intertidal shore platform is visible on the seaward side of the deposit. Pleistocene conglomerates are evident in the upper right-hand portion of the photograph "b". The raised beach deposit is overlain by a thin veneer of sand which also partially covers the conglomerate, but is difficult to discern in this photograph.

occurs within the uppermost part of the matrix of the gravel bed near the contact between the gravel and the overlying sand. A thermoluminescence age of 34.0±2.9 ka (W2317) was previously reported for this sandy unit (Bourman *et al.* 1999). In addition, a radiocarbon age (minimum age) of >30 ka (GaK–6095) has previously been reported for molluscs from the gravel beach deposit (May & Bourman 1984).

Results and Discussion

Mollusc assemblage

The gravel unit contains a relatively diverse assemblage of fossil molluscs, principally gastropods, within the sediment matrix. Molluscs include *Patella (Scutellastra) laticostata* Blainville, *Mactra rufescens* (Lamarck), *Ostrea angasi* Sowerby, *Monodonta (Austrocochlea) constricta* Lamarck, *Nerita (Melanerita) atramentosa* Reeve, *Cymatiella lesueuri* Iredale; *Conus* sp. Linnaeus, *Diloma (Chlorodiloma) adelaidea* (Philippi), *Bembicium melanostoma* (Gmelin), *Sydaphera undulata* (Sowerby) and opercula of *Turbo* sp., Linnaeus. Many of the shells also occur as large fragments, highly abraded and of unrecognizable affinity. Collectively, the fossil assemblage indicates deposition in an environment comparable to the modern coast at southern Sellicks Beach, with molluscs found in sand or attached to rocks, in a relatively sheltered setting of the lower littoral zone (Ludbrook 1984).

Dating

A generally high degree of racemisation (expressed as a D/L ratio) is evident for the five different enantiomeric amino acids measured in each of the fossil molluscs from the gravel beach deposit (Table 1). The relative extent of racemisation for the different amino acids, within the single mollusc samples, generally follows the relation VAL<LEU<GLU<PHE≤ASP. Similar trends are reported for fossil molluscs from United States Pacific coastal plain sites (Lajoie *et al.* 1980).

Three specimens of *Patella (Scutellastra) laticostata* (samples UWGA-695, 696 and 763) reveal good concordance in measured enantiomeric ratios (i.e. between-shell D/L ratio variation) with coefficients of variation less than 5.6% for all amino acids for the combined data (actual values include VAL 2.2%, LEU 5.6%, ASP 0.3%, PHE 1.9% and GLU 5%). The consistently lower degree of racemisation for all amino acids in the specimen of *Patella* sp. (sample UWGA-697), compared with the other three *Patella* samples is possibly due to the diffusive loss of the more highly racemised, lower molecular weight peptide fraction from the shell carbonate matrix. Accordingly, the degree of racemisation as determined in the total acid hydrolysate, would be disproportionately weighted towards the less racemised, higher molecular weight peptide residues that remain within the shell aragonite matrix. This explanation is consistent with the poorly preserved nature of some of the molluscs within the gravel deposit (e.g. chalky appearance).

The high extent of racemisation measured in all the fossil molluscs from the raised beach deposit far exceeds values typically determined in Holocene fossils (Murray-Wallace & Bourman 1990; Murray-Wallace & Goede 1995; Murray-Wallace 2000; Table 1). The extent of racemisation in the molluscs

TABLE 1. *Extent of amino acid racemisation (total acid hydrolysate) in fossil molluscs from a raised gravel beach deposit, Sellicks Beach and other localities for comparison*

Species & Location	Lab. Code or reference	Amino acid D/L ratio[a]				
		VAL	LEU	ASP	PHE	GLU
Sellicks Beach, raised beach deposit						
Thais orbita (columella)	UWGA-733	0.284±0.021	0.369	0.556±0.015	-	-
Sydaphera undulata	UWGA-736	-	0.333	0.322±0.036		-
Patella (Scutellastra) laticostata	UWGA-697	0.309±0.008	0.370±0.018	0.613±0.033	0.541±0.006	0.549±0.051
Patella (Scutellastra) laticostata	UWGA-696	0.412	0.582±0.021	0.800±0.004	0.798±0.029	0.606±0.008
Patella (Scutellastra) laticostata	UWGA-695	0.405±0.003	0.551±0.007	0.799±0.007	0.777±0.017	0.557±0.002
Patella (Scutellastra) laticostata	UWGA-763	0.423±0.008	0.520±0.003	0.804±0.001	0.770±0.009	0.611±0.009
Nerita (Melanerita) atramentosa	UWGA-766	0.386±0.008	0.411±0.000	0.702±0.029	0.599±0.005	0.671±0.006
Ostrea sp.	UWGA-768	0.365±0.010	0.403±0.013	0.835±0.023	0.727±0.008	0.789±0.026
Late Pleistocene, Glanville Formation, Normanville, SA						
Mactra australis	Bourman *et al.* (1999)	0.283±0.011	0.273±0.012	0.590±0.010	-	0.333±0.006
Hindmarsh Island, SA						
Mactra australis		0.26±0.003	0.37±0.002	0.56±0.001		0.36±0.002
Port Wakefield, SA						
Anadara trapezia	Murray-Wallace *et al*	0.32±0.06	0.51±0.02	0.54±0.03	-	0.43±0.01
Katelysia rhytiphora	(1988)	0.32±0.04	0.51±0.07	0.46±0.02	-	0.38±0.04
Holocene						
Three Rivers Creek, King Island, TAS						
Patella laticostata (790±60 yr BP; SUA-2927)	Murray-Wallace & Goede (1995)	0.01	0.05±0.02	-	0.04±0.001	0.05±0.001
Sir Richard Peninsula, SA						
Donax deltoides (22601140 yr BP; SUA-2881)	Murray-Wallace & Bourman (1990)	0.07±0.01	-	0.27±0.01	0.19±0.01	0.12±0.005

[a] amino acids: VAL - valine; LEU - leucine; ASP - aspartic acid, PHE - phenylalanine and GLU - glutamic acid.

from the Sellicks Beach deposit also exceeds that apparent for representative examples from the Late Pleistocene Glanville Formation at Normanville and Hindmarsh Island, two localities with comparable current mean annual air temperatures and, as a corollary, two deposits likely to have experienced similar diagenetic temperature histories to the Sellicks Beach deposit, given the caveat that the shells from each deposit remained buried at depths ≥1 m for much of their diagenetic histories (Murray-Wallace *et al.* 1988; Bourman *et al.* 1999; Table 1). The Glanville Formation, as originally defined in the Adelaide region (Ludbrook 1976; Cann 1978) has been correlated with the last interglacial maximum (125 ka: Oxygen Isotope Substage 5e) based on thermoluminescence, amino acid racemisation and uranium-series dating of correlative deposits from other parts of the South Australian coastline (Belperio *et al.* 1984; Schwebel 1984; Huntley *et al.* 1993, 1994; Murray-Wallace 2000).

Although the fossil molluscs from the raised beach deposit at Sellicks Beach were obtained from near-surface contexts (<50 cm), the geomorphological and stratigraphical evidence suggest that for part of

their diagenetic history, the fossils were more deeply buried (i.e. at least 1 m). However, these molluscs will have experienced a higher integrated diagenetic temperature than for fossils that have remained in more deeply buried contexts (Table 1). Current mean annual air temperatures (CMAT) at Sellicks Beach, Normanville and Hindmarsh Island are all approximately 16° C, and 17° C for Port Wakefield.

The extent of racemisation for the majority of amino acids is significantly higher in the molluscs from Sellicks Beach compared with those from Normanville and Hindmarsh Island (Table 1). The difference in extent of racemisation is less pronounced when compared with the molluscs from Port Wakefield which have experienced a higher diagenetic temperature (Table 1). As current mean annual temperature at the Port Wakefield site is approximately 1° C warmer than at Sellicks Beach, and given that rates of racemisation are known to increase by up to 20 per cent for such a temperature difference (McCoy 1987), the implication is that the shallow burial depth of the shells at Sellicks Beach has contributed to the high degree of racemisation of amino acids within these fossils.

Amino acid D/L ratios for the molluscs from the Sellicks Beach deposit range from the envelope of values representative of last interglacial age to potentially the penultimate interglacial (c. 220 ka; Oxygen Isotope Stage 7), as revealed in a plot of the extent of racemisation against current mean annual temperature (and as a corollary, latitude) (Fig. 7). The lack of clustering and chronological consistency of the data suggests a diagenetic basis for the observed variation in enantiomeric ratios rather than a genuine age variation between shells. The range in D/L ratios for the shells from Sellicks Beach exceeds that typically found for a single isotopic stage (Murray-Wallace 2000).

Although racemisation rates are known to be genus-specific (Miller & Brigham-Grette 1989) this is unlikely to account solely for the higher degree of racemisation in the fossil *Patella (Scutellastra) laticostata* from the Sellicks Beach deposit, compared with other genera from the Glanville Formation. It is therefore concluded that the higher degree of racemisation in the molluscs from Sellicks Beach is due to faster rates of racemisation, due to their shallow burial depth during late diagenesis resulting from the progressive exhumation of the deposit, and a genus-effect on racemisation.

As the shells have been subjected to variable burial depths during late diagenesis, the integrated rate expression for racemisation was rearranged with temperature as the subject to assess whether it is possible to induce the high extent of racemisation at ambient diagenetic temperatures over the course of the Holocene. As the amino acid analyses reported

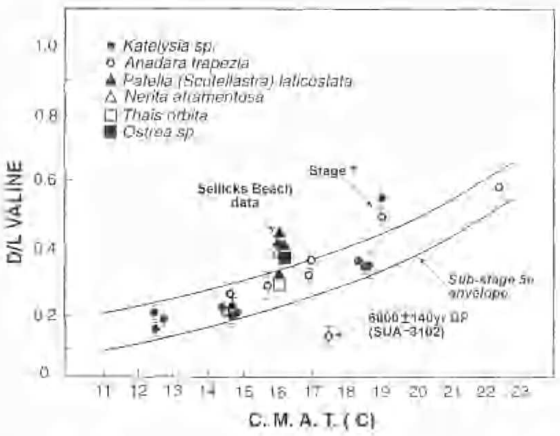

Fig. 7. The extent of valine racemisation (total acid hydrolysate) in fossil molluscs of last interglacial age (Oxygen Isotope Substage 5e) from southern Australia plotted against current mean annual air temperature (° C) to illustrate the Sellicks Beach data within a broader, regional context. Details of samples from elsewhere in southern Australia are reported by Murray-Wallace & Belperio (1991) and Murray-Wallace *et al.* (1999). The amino acid data for the last interglacial molluscs are in accord with the exponential trend of increasing extent of racemisation with higher diagenetic temperatures, and as a corollary, higher current mean annual temperatures. The fossil molluscs from the raised beach deposit at Sellicks Beach reveal a broad range in extent of racemisation from the envelope of the last interglacial to values consistent with a penultimate interglacial age (Oxygen Isotope Stage 7, c. 220 ka). Amino acid results for Holocene and Stage 7 molluscs are presented as a framework for comparison.

here were undertaken on different fossils from those used for the radiocarbon assay (~30 ka age; May & Bourman 1984), the integrated diagenetic temperature was calculated to examine the possibility that the radiocarbon age was the result of chance sampling of reworked Pleistocene shells within a Holocene deposit. A minimum age of 7000 years was selected for the calculation, representing the timing of the culmination of the post-glacial marine transgression in southern Australia (Belperio *et al.* 2002), and, therefore, the oldest age likely for an undisturbed Holocene coastal deposit. The rationale for this is that the early Holocene is the only time in the Late Quaternary, apart from the last interglacial maximum, that sea level was sufficiently high potentially to form the raised beach. Present sea level is not sufficiently high to form the deposit. Furthermore, interstadial sea levels of the Late Pleistocene (Chappell *et al.* 1996) were significantly below present sea level and would imply rates of tectonic uplift of a magnitude inconsistent with the

well-established tectonic framework for the region (Bourman *et al.* 1999; Belperio *et al.* 2002).

An average diagenetic temperature required to induce the degree of racemisation measured in the fossils assuming an age of 7 ka was determined thus:

$$T = \frac{5939}{15.77 - \log_e \ln\left[\frac{(1+D/L)}{(1-D/L)f}\right] - \ln\left[\frac{(1+D/L)}{(1-D/L)lo}\right]}{2t}$$

where T is the absolute temperature (°K), D/L_f and D/L_{lo} are the enantiomeric ratios of the fossils and their modern equivalents respectively, t is an assumed age (i.e. 7000 years) and 15.77 and 5939 are constants derived from the empirical rate constant expression (Wehmiller 1982, 1993). Accordingly, an average diagenetic temperature of 24° C would be necessary to induce the extent of racemisation measured in the three specimens of *Patella (Scutellastra) laticostata* (UWGA-695, -696 and -763) from the raised beach deposit if they were only 7 ka. A diagenetic temperature of this value is unlikely, however, given that the current mean annual air temperature at Sellicks Beach is approximately 16° C. A prolonged, higher mean annual temperature by as much as 8° C is unlikely over the course of the Holocene for this region (Chappell 1991). Thus, the extent of racemisation measured in the fossil molluscs from the raised beach deposit could not have been attained during the Holocene. A penultimate interglacial age is also not favoured, as the gravel beach deposit is unlikely to have survived erosional processes of the last two glacial cycles. On this basis a last interglacial age is favoured for the raised gravel beach deposit at Sellicks Beach.

Neotectonics

The raised gravel beach deposit at Sellicks Beach provides a further opportunity to examine the neotectonic behaviour of Fleurieu Peninsula. Previous investigations have revealed that the region has experienced geologically recent uplift as indicated by the elevation of last interglacial coastal deposits (Bourman *et al.* 1999).

Although many gravel beach deposits represent relational sea-level indicators (i.e. always form above tidal datum) and are therefore of only modest reliability (Chappell 1987), several attributes of the deposit at Sellicks Beach render it more reliable for quantifying rates of neotectonism. The adjacent modern intertidal platform has clearly formed within a narrow range of tidal datum and represents an analogous feature to the Pleistocene equivalent. The upper reaches of the modern shore platform are covered by boulders and cobbles presumably accumulated during storm events. However, the steep backing slope of the cliff prevents boulders or finer clasts from being deposited at any significantly higher elevation above tidal datum.

Estimates of a glacio-eustatic sea level for the last interglacial (Oxygen Isotope Substage 5e) from Eyre Peninsula suggest a value of 2 m AHD, and represents a particularly reliable datum given the relative tectonic stability of the Gawler Craton upon which much of the Eyre Peninsula coastline has developed (Murray-Wallace & Belperio 1991). Thus, uplift of the Sellicks Beach deposit by as much as 3 m is indicated based on the elevation of the contact between the gravel deposit and the underlying erosional surface of the relict shore platform.

The amount of uplift since the last interglacial maximum, inferred from the deposit at Sellicks Beach (c. 3 m) is less than that observed at Normanville (c. 10 m) to the south of the Willunga Fault (Bourman *et al.* 1999). The uplift is attributed to the combined effects of ongoing tectonic uplift of the Adelaide Hills and erosional unloading and associated crustal isostatic compensation. Further research is required to model these processes geophysically.

Conclusions

The extent of racemisation for several amino acids in fossil molluscs from a raised gravel beach deposit at Sellicks Beach, South Australia, indicates that the deposit is of Late Pleistocene age, and most likely formed during the last interglacial maximum (c. 125 ka; Oxygen Isotope Substage 5e). The deposit indicates up to 3 m of uplift has occurred in this region since the last interglacial and suggests that the region is still undergoing neotectonic uplift.

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